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NAVORD REPORT

6641

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HEAT RESISTANT EXPLOSIVES VII (U)

SYNTHESIS AND ANALYSIS OF POTASSIUM-2,2',4,4',6,6'-HEXANITRODIPHENYLAMINE (U)



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HEAT RESISTANT EXPLOSIVES VII (U)
SYNTHESIS AND ANALYSIS OF
POTASSIUM-2,2',4,4',6,6'-HEXANITRODIPHENYLAMINE (C)

312545

Prepared by:

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ABSTRACT: The potassium salt of 2,2',4,4',6,6'-hexanitrodiphenylamine (KHND) may be prepared from 2,2',4,4',6,6'-hexanitrodiphenylamine (HND) and potassium acetate in good yield by reaction in methanol-acetone solution at room temperature. The product is precipitated by addition of water followed by cooling. Preparations by this procedure give a very pure product which has excellent thermal stability at 260°C.

KHND may be analyzed potentiometrically, spectrophotometrically, or gravimetrically, a potentiometric titration with standard hydrochloric acid in water being preferred. HND as an impurity in KHND may be determined potentiometrically by titration in acetone with aqueous sodium hydroxide.

The pk of HND in water at 28°C is 2.71 ± 0.02 (zero ionic strength).

CHEMISTRY RESEARCH DEPARTMENT
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This report describes the synthesis and analysis of potassium-2,2',4,4',6,6'-hexanitrodiphenylamine, a new explosive with excellent thermal stability at 260°C. NavOrd Reports 6016, 6017, 6208, 6223, 6225 and 6299 are the preceding reports on heat resistant explosives.

The work was performed under Task 301-664/43006/08. Although the preparative work was carried out on a 100 gram scale, there is reason to believe the method can be scaled to plant production without loss of quality or yield. The method of analysis worked out would be applicable for quality control purposes.

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Captain, USN
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for *ALH*
ALBERT LIGHTBODY
By direction

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SYNTHESIS AND ANALYSIS OF
POTASSIUM-2,2',4,4',6,6'-HEXANITRODIPHENYLAMINE (C)

PART I

Synthesis of Potassium Hexanitrodiphenylamine, KHND

INTRODUCTION

Several guiding principles have been used in searching for explosives with improved heat stability. In the first place, all chemical bonds in the molecule should be as strong as possible, indicating the desirability of nitro groups attached to a carbon skeleton with which they can resonate.

A high melting point is also desirable in a high temperature resistant explosive, both because melting would produce an expansion awkward to accommodate in a weapon and because molten or dissolved explosives decompose more rapidly than they do in the crystal. Strong intermolecular forces are thus desirable. The possibilities of increasing the crystal lattice energy include ionic structures, hydrogen bonding, molecular symmetry and large molecular size. In general nitro groups do not form strong hydrogen bonds in spite of the large dipole moment, but this might be overcome by giving the molecules the opportunity of forming a number of them.

These guiding principles have been startlingly successful, as they lead to the discovery of the remarkable temperature resistance of the polyaminotrinitrobenzenes. Dr. J. M. Rosen of this laboratory also pointed out that 2,2',4,4',6,6'-hexanitrodiphenylamine, HND, melting at 243° to 244.5° , should be included in this group. As HND offered no advantages over DATB (1) or TATB (2), Dr. Rosen suggested investigation of the metallic salts of HND, as they should be high melting and might have sensitivities in the booster explosive range. The potassium salt is only slightly soluble in water (3) and was selected for investigation first, as its sensitivity is essentially the same as that of tetryl.

The explosive properties of potassium-2,2',4,4',6,6'-hexanitrodiphenylamine, KHND, are not reported in the literature. However, crystalline compounds of HND with potassium, rubidium, and cesium are used for the microchemical detection of these elements (3).

DISCUSSION AND RESULTS

The first samples of KHND were prepared by suspending HND in alcohol to which was added dropwise an aqueous solution of potassium acetate in ten, twenty, and one hundred fold excess. The red crystalline KHND samples were recrystallized by dissolving in acetone and reprecipitating by adding water. These samples produced from 8 to 18 cc. of gas per gram per hour at 260°C (500°F). Repeated recrystallizations did not significantly improve the thermal stability.

It was believed that a better quality product would result from carrying out the reaction in a homogeneous system. This idea was verified by the following experiment. A sample of KHND with poor thermal stability (18 cc/g/hr at 260°C) was dissolved in acetone to which was added a solution of potassium acetate in acetone-methanol. The mixture was stirred for thirty minutes, diluted with water and chilled. The KHND was isolated and dried and the thermal stability re-run. The thermal stability was 1.7 cc of gas/g/ hr at 260°C.

A sample of KHND was assayed both before and after reworking by the above mentioned procedure. The assay of the KHND before reworking showed it to be only 93 mole percent pure after reworking. The analysis showed the chief impurity was unreacted HND, which would account for its instability at 260°C.

A ten gram sample of KHND was prepared in acetone solution using equal molar quantities of HND and potassium acetate. The crude KHND as isolated from the reaction mixture was 99.7 mole percent pure and gave 3.9 cc of gas/g/hr at 260°C.

One sample of KHND was prepared by dissolving the HND in dilute sodium hydroxide and treating with aqueous potassium bromide. The KHND precipitated immediately. When this sample was heated in the vacuum stability block at 260°C, it gave 6.0 cc of gas/g/hr.

The cook-off temperature of KHND was measured by exposing a copper cased 1/2" x 1/2" cylinder loaded with KHND to a rapid air stream at 310°C. Under these conditions HMX "cooked-off" in 7.8 minutes while 19.5 minutes was required by KHND (4).

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Studies related to the physical, chemical, and explosive properties of KHND are continuing at these laboratories. Some additional work is being carried out by the Universal Match Corporation on a Navy contract, NO. N123(62738)18698A.

We plan to make other metal salts of HND, since it is believed they will also be heat resistant. It is believed that the heavy metal salts will be more sensitive to impact than KHND. Thus we hope to be able to supply the fuze train designers with a variety of heat resistant explosives.

The physical properties of KHND are compared with tetryl in Table I. The detonation velocity measurements and the effect of temperature on gap sensitivity are given in Table II, and it is noted that the critical gap length at -60°C is only slightly shorter than at ambient temperature, but that it is about double at 180°C . Preliminary measurements by Rosen showed that KHND underwent a polymorphic change at about 170°C and it is possible that this is the reason for the marked difference in sensitivity at 180°C (5). This is being investigated by Hampton of these laboratories.

EXPERIMENTAL

Preparation of Potassium-2,2',4,4',6,6'-hexanitrodiphenylamine

A three gallon Pyrex bottle was charged with 100 grams (0.27 mole) of HND, 1500 ml of acetone, and solution containing 40 grams (0.4 mole) of potassium acetate in 250 ml of methanol and 100 ml of acetone. The mixture was shaken by hand until solution was complete and then allowed to stand at ambient temperature for an hour. The reaction mixture was diluted to the capacity of the bottle with water and chilled at -10 to -20°C overnight. The supernatant liquid was siphoned off and the red crystalline KHND collected on a Buchner funnel. The product was washed with water, sucked dry on the funnel, and the drying completed in vacuo at 70°C . The yield of KHND was 119.0 grams, 93% of theory based on HND.

KHND like tetryl has a strong coloring action on human skin. KHND has been reported to give dermatitis to operators at both the Naval Ordnance Laboratory and the Universal Match Corporation. Solutions of KHND appear to cause the most trouble. Great care should be exercised to keep the solution off of the skin.

We recommend that personnel handling KHND wear protective clothing, especially rubber gloves, and that the work area be thoroughly cleaned after each operation. We feel that if the basic principles of good laboratory technique and good housekeeping are adhered to there will be no difficulty in working with KHND.

CONCLUSIONS

We can readily prepare research quantities of KHND that are extremely pure and thermally stable at 260°C.

ACKNOWLEDGMENTS

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TABLE I
PHYSICAL PROPERTIES OF KHND AND TETRYL

Compound	m.p.	Impact Sensitivity in cm -2.5kg wt	Vacuum Stability cc gas/48 hrs at 100°C/g	Crystal Density g/cc
KHND	>400°C	26	<0.10	1.85
Tetryl	129°C	32	0.14 EC*	1.73

* Denotes that the gas volume exceeded the capacity of the apparatus which is 30 cc. Tetryl decomposes very rapidly above its melting point.

TABLE II

DETONATION VELOCITY MEASUREMENTS OF
POTASSIUM-2,2',4,4',6,6'-HEXANITRODIPHENYLAMINE

<u>Density</u>	<u>Velocity (Meters/Sec.)</u>
1.14	4970
1.56	6279
1.72	6919 (93% of crystal density)*

* Tetryl, 7750 m/sec. at 1.60, 92.6% of
crystal density (6,7).

EFFECT OF TEMPERATURE ON GAP SENSITIVITY(8)

(Air Gap in Inches)

<u>Explosive</u>	<u>-60°C</u>	<u>Ambient Temp.</u>	<u>+180°C</u>
KHND	0.094	0.110	0.222
Tetryl	0.096	0.127	0.156(100°C)

REFERENCES

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- (2) Kaplan, L. A. and Taylor, Francis, Jr., NavOrd Report 6017, High Temperature Stable Explosives I, Process Development Study of 1,3,5-Triamino-2,4,6-Trinitrobenzene, March 1958. (C)
- (3) Welcher, F. J., Organic Analytical Reagents, Vol. IV, D. Van Nostrand Co., Inc., New York, New York, 1948.
- (4) Riel, G., Stresau, R. H. F., and Slie, W. M., NavOrd Report 4383, Cook-Off Studies of the Booster XW-7 and Variants, October 1957. (C)
- (5) Private Communication from Dr. J. M. Rosen of these laboratories.
- (6) Hampton, L. D., NavOrd Report 3731, Small Scale Detonation Velocity Measurement from May 1951 to May 1954, June 1954. (C)
- (7) Hampton, L. D., data will be published in a future NavOrd Report.
- (8) Ibid.

PART II

INTRODUCTION

HND, dipicrylamine, is used for the quantitative determination of potassium in aqueous solution. Generally, the magnesium salt of HND is used to precipitate the insoluble potassium salt which usually is filtered, washed, and weighed as such. Variations in the determination are reviewed by Welcher (1) and include determination of the potassium salt after solution in acetone-water by (a) conductometric titration with standard hydrochloric acid (2); (b) acidimetric titration of excess standard hydrochloric acid used to precipitate HND (after removal of acetone by boiling) (3); (c) colorimetric determination after dilution with water containing sodium hydroxide (3); and (d) acidimetric titration with standard hydrochloric acid to the disappearance of the red color (5). Also included is a method based on reduction of the nitro groups by titanous ion (4).

Some of these methods were tried, but were found unsatisfactory for various reasons. In this laboratory it was found that a potentiometric titration of the potassium salt with standard hydrochloric acid gave the most satisfactory results for an accurate assay, and a potentiometric titration with standard sodium hydroxide was best for determining the major impurity.

SELECTION OF A METHOD AND RESULTS

Titrimetric with Visual End Point

The titrimetric procedure using standard hydrochloric acid as a titrant without an added indicator was tried first (5). The end point was decidedly improved in the absence of acetone, presumably due to the almost complete removal of the anion by precipitation as HND. The potassium salt has a solubility of 0.88 g/l in water at 25°C, while the solubility of HND is 0.0064 g/l. The procedure was tested by using small amounts of pure HND in the presence of excess standard sodium hydroxide. When the procedure was used with the potassium salt prepared as described above, (Table I, 4969-160), an indicated purity of 99.9% was found. In view of the vacuum stability results, the purity could not be this good and, consequently, the method was assumed to be unreliable.

Gravimetric

Because of the insolubility of HND in water containing excess acid, the next procedure consisted of determining the amount of HND precipitated by adding excess concentrated hydrochloric acid to a solution of the potassium salt. This procedure indicated a purity of 100.3% for sample 4969-160. This high result tended to confirm the suspected presence of HND as the impurity. (Note that % purity = $\frac{477.3 \text{ (g precipitate)}}{439.2 \text{ (g sample)}}(100)$, where 477.3 is the formula weight of the potassium salt and 439.2 is the formula weight of HND.)

Spectrophotometric

The spectrum of KHND was determined in several solvents and, contrary to the literature (3), Beer's law was found to hold at the maximum. Sample 4969-160 was analyzed spectrophotometrically in acetone to give a value for the purity of $99.5 \pm 1.0\%$. The spectrum of HND in a given solvent showed that with increasing dilution the maximum was shifting towards longer wavelengths until the maximum for the anion was obtained. This data indicated that the acid was essentially completely ionized at the dilutions ($10^{-5}M$) used for analyzing the salt. Inasmuch as the spectrum of 4969-160 was the same as the pure salt, the analysis showed that HND was the likely impurity in the salt.

The data for HND also showed how it could interfere in the titrimetric procedure. Because the titration was carried to the disappearance of the red color, any dissolved HND would be titrated due to its being ionized.

Isolation of HND as Impurity

Test tube experiments indicated that solution of HND in water was not at all fast. Consequently, a sample of the questionable potassium salt, 4969-160, on a sintered-glass crucible was extracted with boiling water until the solution was no longer red. There remained a yellow crystalline solid, which when dried and weighed proved to be 6.46% of the starting material. A repeat of this experiment with water at $50-60^{\circ}C$ required about twice as much water for the same sample size, and left a residue amounting to 6.09%.

The residue had a melting point of $241-2^{\circ}$ and did not depress the melting point of a pure sample of HND. Thus, the potassium salt was at best 93.7% pure and contained HND as the major impurity.

Potentiometric Titration of HND and Its Potassium Salt

The insolubility of HND in water suggested the potentiometric titration of the potassium salt, KHND, for such a titration would not suffer the disadvantage of the visual end point (see also, ref. (7)). A plot of a typical titration of the pure salt using standard hydrochloric acid as titrant is given in Figure 1. The end point, $\text{pH}=4.88$ at 33°C , was taken as the mid point of the steep part of the curve. The end point pH at 25°C is 5.60. Such a titration with the salt containing 6.3% HND gave 92.6% as the purity. The titration was slow, apparently due to the absorption of the titrant on the HND. The speed was improved, and the end point sharpened by using benzene to dissolve the HND as it formed. With benzene present, the end point pH was 5.25, 5.07, and 4.73 at 25, 30, and 35°C , respectively.

Inasmuch as HND was the major impurity, it was desirable to be able to determine it as such in the potassium salt. Titration as an acid with standard base seemed most logical, but the insolubility of HND in water made potentiometric titration in this solvent difficult. It was found that HND in acetone could be potentiometrically titrated with standard aqueous sodium hydroxide to give an easily discernible end point. The plot "pH" versus "ml of sodium hydroxide added" gave a curve similar to that for the titration of hydrochloric acid (Figure 2). This data indicated that instead of being a weak acid (3,7) HND was probably as strong as hydrochloric, at least in acetone-water solutions.

Titration of KHND, sample 4969-160, in acetone with standard sodium hydroxide showed that it contained 6.23% acid as unreacted HND, which is in good agreement with 6.3% found by the aqueous extraction previously described.

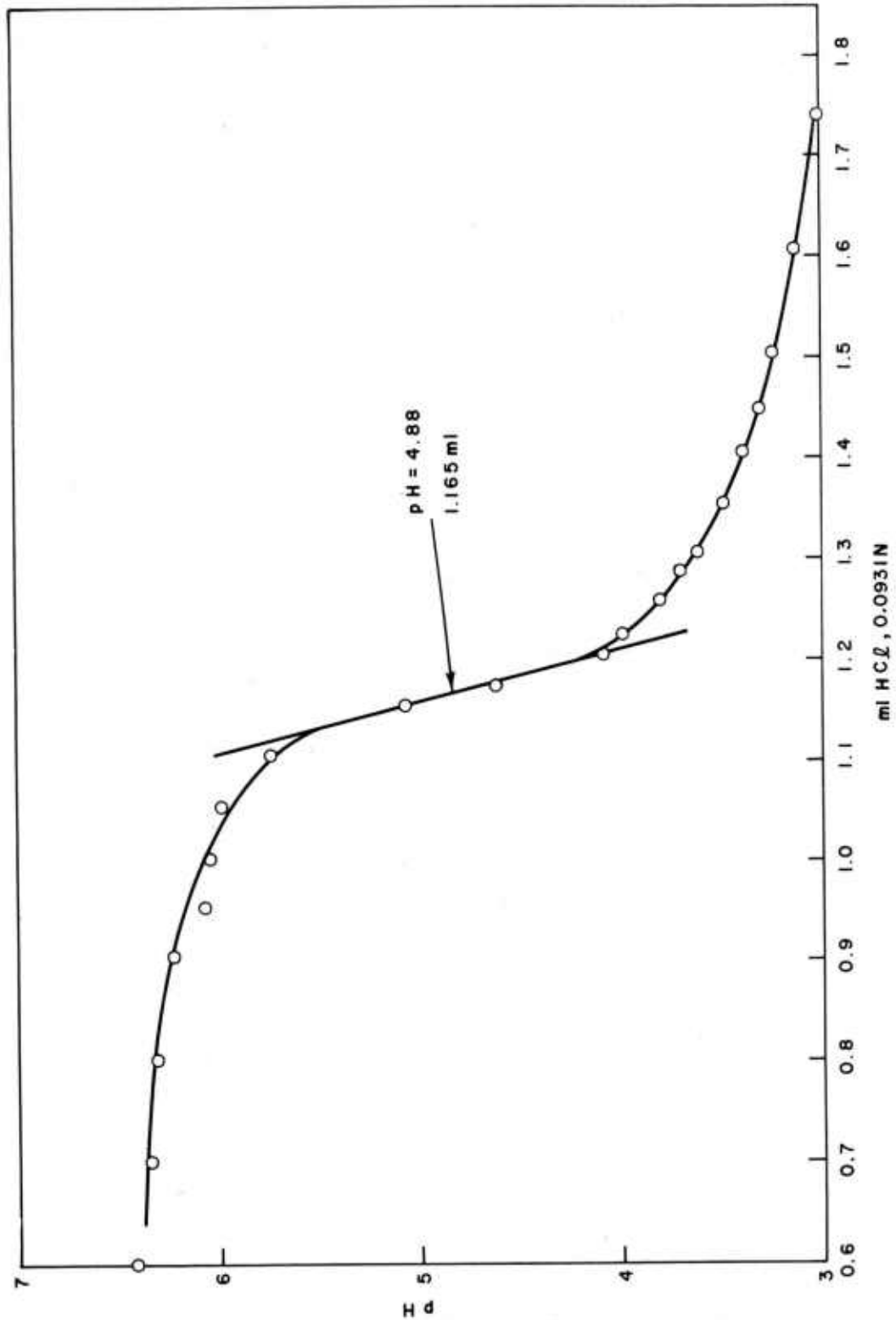


FIG. 1 TITRATION OF KHND IN WATER
WITH HYDROCHLORIC ACID AT 33°C

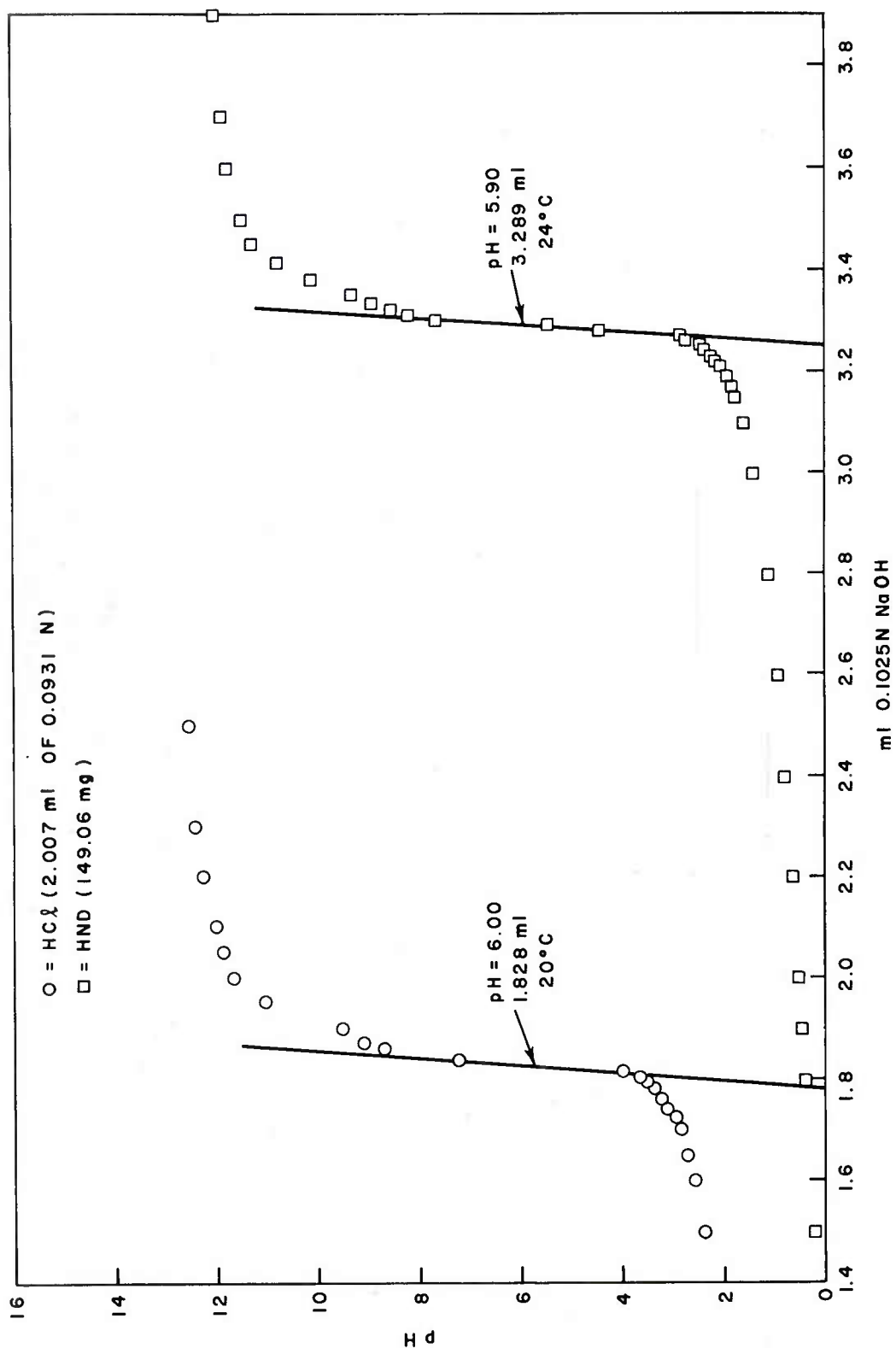


FIG. 2 TITRATION OF HND AND HCl
IN ACETONE WITH NaOH

Analytical Results and Other Impurities

HND was not the only impurity found in the potassium salt. In general, analyses were made only on samples which did not give good vacuum stability results. Three other impurities were thus found. The first, solvent, was eliminated by increasing the drying time under vacuum. The second impurity was an oil which had been inadvertently introduced with the alcohol used as solvent. As only a few preparations were made using this batch of alcohol, this impurity was removed by washing and the impure alcohol discarded.

The third impurity was 2,2',4,4',6-pentanitrodiphenylamine. As the purity of the HND was usually quite good, it was used as received to prepare KHND. On one occasion this led to a product having very poor vacuum stability. A melting point determination on the starting material showed it to be impure and a potentiometric titration of a sample with sodium hydroxide in acetone gave two distinct breaks, indicating two acids of different strength. In order to separate the two breaks for quantitative analysis, a potentiometric titration was carried out in dioxane-water and it was found that the neutralization equivalent of the impurity was 403 in good agreement with the calculated value of 394 for the pentanitro compound. A potentiometric determination of the potassium salt prepared from this impure HND, with sodium hydroxide in acetone, showed that the weaker acid was present as free acid. When the potassium salt was dissolved in water an insoluble yellow solid remained. The spectrum of this solid in absolute ethanol (acidified) agreed very well with that for the pentanitro compound reported in the literature(10), (see experimental).

The results of analyses on the various preparations of the KHND are given in Table I.

DISCUSSION OF ANALYTICAL RESULTS

From Table I a comparison of the various analytical methods can be made. It is suggested that the potassium salt, prepared by the procedure described in this report, should be analyzed only if vacuum stability results warrant it. As the most likely impurity is HND, a potentiometric analysis in acetone using standard sodium hydroxide should be made. Solvent and other non-acidic impurities will be

indicated by the potentiometric titration of the salt in water with standard hydrochloric acid. For routine analyses on large scale preparations, the spectrophotometric method using water as solvent will probably be satisfactory. This determination will show the presence of reasonable amounts of HND or its precursors by their insolubility and, consequently, show the necessity for the potentiometric determinations.

KHND may also be determined by extraction with hot water from water-insoluble impurities such as HND.

TABLE I
QUANTITATIVE ANALYSIS OF KHND

Sample	% KHND		% HND		Vacuum Stability cc gas/g/hr. at 260°C
	Spectro. ± 1.0% /a	Potentio. ± 0.2% /a	Gravi. ± 0.1% /a	Potentio- metric /a	Gravi- metric /a
KHND, recryst.	100.0 /b	99.4	/c	-	-
HND, recryst.	-	-	-	99.5 ± 0.6	-
4969-160	99.5 /d	92.6	100.3	6.23 ± 0.06	6.28 ± 0.19
4969-161	-	96.3	-	0	-
4970-2 /e	-	98.5	-	0	-
4970-2, redried	-	100.2	-	-	-
4970-3	-	96.6	-	0	-
4970-3, redried	-	99.7	-	-	-
4970-5 /f	96.6 /g	97.8	99.8	0	-
4970-7 /f	95.0 /g	96.0	98.6	0	-
4970-8 /f	97.1 /g	96.8	98.8	0	-
4970-103	81.0 /h	81.2 /h	-	17.7 /i	-

/a Average deviation on duplicate

/b Standard

/c See reference (3)

/d Solvent, acetone

/e This sample is reworked 4969-160

/f Impurity shown to be an oil

/g Solvent, water

/h In water, after filtering insoluble yellow solid (10.1%)

/i This is % of 2,2',4,4',6-pentanitrodiphenylamine

pk DETERMINATION IN WATER

There is some considerable difference of opinion in the literature as to the strength of HND as an acid. At present, the pk of HND in various solvents is being determined in this laboratory and will be reported at a later time. The results in water will be reported here.

The titration of the sodium salt of HND in water at 20°C with standard hydrochloric acid was reported by Treadwell and Hepenstrick (7). They titrated 273.2 mg of the salt (5.80×10^{-4} moles) with 0.4994N hydrochloric acid (aqueous) and found that pH at the equivalent point to be 5.19 and the pH at "half titration" to be 8.15. From this result, they report k as $10^{-8.15} = 7.08 \times 10^{-9}$. It is difficult to reconcile this value with the fact that HND is so very insoluble in water. Unfortunately, the initial volume of water used in the above titration is not given. However, for the anion concentration to be equal to the HND concentration (1.2×10^{-5} M) at half titration, one can calculate that the volume of solution must have been better than 24 liters ($2.9 \times 10^{-4} / 1.2 \times 10^{-5} = 24$), which is not reasonable. Consequently, one must conclude that the insolubility of HND was not taken into account and at half titration, the concentration of anion was considerably greater than the HND concentration.

Still another value of k_1 in water at 25°C is reported by Pan and Lin (6). They note that the solubility of HND is 1.45×10^{-5} M and they find that the pH of a saturated solution is 5.2. Therefore, they report that k_1 is 4.9×10^{-6} . Presumably, this value is calculated by assuming $(H^+) = (\text{Anion}) = 6.31 \times 10^{-6}$, and $(\text{HND}) = (14.5 - 6.31) \times 10^{-6}$, from which $k_1 = (6.31 \times 10^{-6})^2 / 8.2 \times 10^{-6} = 4.85 \times 10^{-6}$.

A pk value of 0.35 is reported for HND in dioxane (8). This value would seem rather low, for usually the pk of an acid of this type increases on going from water to organic solvents. Apparently, the value of 0.35 is in fact the pH meter reading in dioxane-ethanol at half neutralization.

In this laboratory, the pk of HND in water at 28°C was determined as follows:

To a known concentration of the anion was added aliquots of a standard solution of hydrochloric acid, and the resulting anion concentration was determined spectrophotometrically. The HND concentration was determined by difference, and the (H^+) was assumed to be equal to the added hydrochloric acid concentration. These values of pk were plotted versus ionic strength and the pk at zero ionic strength was found to be 2.71 ± 0.02 (Table II).

TABLE II

pk OF HND IN WATER AT 28°C BY
SPECTROPHOTOMETRIC MEASUREMENTS
ADDED ANION CONCENTRATION = $1.040 \times 10^{-6}M$

pH <u>/a</u>	Molarity			pk HND	μ 1/2
	HCl <u>/b</u>	Anion	HND		
1.95	93.1×10^{-4}	2.14×10^{-7}	8.26×10^{-7}	2.62	0.0965
2.93	9.31 "	7.23 "	3.17 "	2.67	0.0305
4.02	0.931 "	9.94 "	0.46 "	2.70	0.00965
-	-	-	-	2.71	0

/a Measured

/b Used for hydrogen ion concentration

EXPERIMENTAL

Apparatus

Absorbancy readings were made with a Beckman spectrophotometer, model DU, using quartz cells with a 1 cm or 10 cm light path.

A Beckman model G pH meter was used for pH measurements.

Reagents

Eastman White Label HND was used as is and also recrystallized by dissolving it in acetone and precipitating it with ether. This product melted at $241-243^{\circ}\text{C}$.

KHND as prepared in Part I was recrystallized from water.

Standard hydrochloric acid and sodium hydroxide were prepared in the usual manner.

All solvents were C.P. or Reagent grade. Distilled water was used throughout.

Analytical Procedures

Titrimetric with Visual End Point

4969-161 KHND, 0.16932 g, was dissolved in 50 ml of distilled water by heating. This solution was titrated while hot to about 90% of the calculated value. The solution was cooled to room temperature and the titration continued to the disappearance of the red color. Required, 3.800 ml of 0.0931 N HCl. KHND, mg found, $3.800(0.0931)(477.3) = 168.9$.

Gravimetric

The titration described above was repeated on a 69.592 mg sample of KHND. At the end of the titration, 1 ml of concentrated hydrochloric acid was added to the solution (which became completely colorless) and the yellow precipitate was filtered onto a previously weighed, medium porosity, sintered-glass crucible. The precipitate was washed with three 10 ml portions of water and dried at 60°C for 2 hours.

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HND: Calcd., $\frac{439.2(69.592)}{477.3} = 64.037 \text{ mg};$

Found, 64.237 mg (100.3%)

Spectrophotometric

Spectral data in water is given under "pk Determination in Water."

The spectrum of KHND (recryst.) in acetone showed a maximum at 418 m μ , $a_m = 2.95 \times 10^4$. The location of the minimum could not be found because of solvent absorption below 325m μ , but the minimum appears to be near 330m μ ($a_m = 1.00 \times 10^4$).

A 1.370 mg sample of KHND was dissolved in acetone in a 25 ml volumetric flask and the solution was diluted to volume with acetone. This solution was diluted by 1/5 and the absorbancy of the latter solution versus acetone at 418m μ was 0.670.

KHND found, $\frac{0.670}{2.95 \times 10^4} \frac{(5)(477.3)(1000)}{(40)} = 1.355 \text{ mg (99.0\%)}$

Isolation of HND as an Impurity

A 0.80643 g sample of KHND was weighed onto a previously weighed, medium porosity, sintered-glass crucible. With no suction applied, the crucible was filled (12.5 ml) with boiling water. After about one minute, the aspirator was turned on and the water pulled through the crucible. A total of 13 fillings with water were required before the red color was no longer evident. The crucible and the yellow solid residue were dried at 50°C for one hour, giving 52.19 mg of residue. After washing with two 12.5 ml portions of water and again drying, the residue weighed 52.11 mg. This was 6.46% of the original sample.

Isolation and Determination of 2,2',4,4',6-pentanitrodiphenylamine

A sample of lot 25 of Eastman White Label HND weighing 88.745 mg was dissolved in 10 ml of dioxane and titrated with 0.1026 N sodium hydroxide potentiometrically. The first break in the titration curve came at 1.642 ml, corresponding to 74.0 mg of HND. The second break came at 1.998 ml, corresponding to 0.03652 meq. $((1.998-1.642)(.1026))$. From this value, the neutralization equivalent was found to be 403 $((88.7-74.0)/0.03652)$.

A sample of KHND, 4970-103 (Table I), weighing 56.191 mg was heated in a 100 ml volumetric flask with 80 ml of water, and after cooling to room temperature the solution was diluted to volume with water. There remained a yellow solid which when filtered and dried weighed 5.679 mg (10.1%) and melted at 194-5°C. A 50.00 ml aliquot of the solution was titrated with 0.0931 N hydrochloric acid potentiometrically, requiring 0.513 ml. This corresponds to 45.60 mg KHND in the 100 ml solution which was 81.2% of the starting material. The spectrum of the solid in absolute ethanol (containing 0.01 ml of concentrated hydrochloric acid per 10 ml of solution) showed maxima at 391m μ and 307m μ with molar absorbandy indexes of 1.87×10^4 and 1.14×10^4 , respectively, based on the material being pentanitrodiphenylamine. The literature (10) values for this compound in this solvent are (max., molar abs.): 392m μ , 1.89×10^4 ; 308m μ , 1.07×10^4 .

Potentiometric Titration of KHND and HND

KHND

A 52.102 mg sample of recrystallized KHND was dissolved in 50 ml of water by warming to 50°C, and 0.0931 N HCl was added in increments to the stirred solution as it cooled. The stirring was stopped for pH readings. After adding 0.502 ml of hydrochloric acid, the temperature was 35°C and the pH was 6.45. A total of 1.749 ml of hydrochloric acid was added and the final pH was 3.00 at 33°C. The plot of pH versus ml of hydrochloric acid is given in Figure 1, from which the end point was determined as 1.165 ml at pH = 4.88. KHND found, $1.165(0.0931)(477.3) = 51.76$ mg (99.3%).

In later determinations, a volume of benzene equal to the water was added before titrating.

HND

A sample of Eastman White Label HND weighing 0.14906 g was dissolved in 25 ml of acetone and 1 ml of water added. The titration was done at room temperature (24°C), and the results are plotted in Figure 2. The end point was at pH reading of 5.90, corresponding to 3.289 ml of 0.1025 N sodium hydroxide.

HND found, $0.1025(3.289)(439.2) = 148.1 \text{ mg } (99.3\%)$.

pk Determination in Water

The spectrum of KHND in water showed a maximum at 428m μ , $a_m = 2.60 \times 10^4$ and a minimum at 295m μ , $a_m = 0.66 \times 10^4$. In solvents other than water, the maximum for HND (unionized) is generally at 370-380m μ with a molar absorbancy near one-half that of the anion at its maximum. Furthermore, although the anion still absorbs strongly at 500m μ , the unionized acid does not. Consequently, the anion concentration in a solution containing both can usually be determined at the longer wavelengths without interference by HND.

In the present determination, a solution of KHND was prepared by dissolving 24.831 mg in boiled distilled water in a 100 ml volumetric flask and diluting the solution to volume with water. This solution was diluted by 1/10 to give a KHND solution 5.20×10^{-5} M. For the pk determination, four solutions were prepared from the latter solution as follows:

To 2 ml of the 5.20×10^{-5} M solution pipetted into a 100 ml volumetric flask, was added water to about 85 ml. To three such solutions, 10.00 ml, 1.00 ml, and 0.1000 ml of 0.0931 N hydrochloric acid were added, while to a fourth solution was added 0.1 ml of 0.1026 N sodium hydroxide. These solutions were diluted to volume with water and mixed.

The absorbancies of each of the solutions were determined in a 10 cm spectrophotometer cell from 520m μ through 290m μ at 10m μ intervals. Assuming no absorbancy due to HND, the percent of HND ionized was calculated for each reading based on the absorbancies of the solution containing sodium hydroxide. The values so calculated were constant above 430m μ (Table III) and increased below this wavelength, indicating that HND did

not interfere above 430m μ . The hydrochloric acid solutions, which were 9.31×10^{-3} M, 9.31×10^{-4} M, and 9.31×10^{-5} M, were found to be in order, 20.6, 69.5, and 95.5% ionized with respect to HND. The pk values are given in Table III.

TABLE III
IONIZATION OF HND IN
HYDROCHLORIC ACID SOLUTIONS

Wavelength m μ	HND, % Ionized		
	M, HCl		
	9.31×10^{-5}	9.31×10^{-4}	9.31×10^{-3}
520	-	-	22.0
510	95.2	71.4	21.4
500	96.4	71.6	22.0
490	95.7	69.0	20.9
480	94.1	69.2	19.5
470	96.0	69.9	19.1
460	95.2	68.2	19.9
450	95.2	68.1	19.8
440	94.7	68.0	20.6
430	96.6	70.5	-
Average	95.5	69.5	20.6
Av. dev.	± 0.6	± 1.0	± 0.9

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8 May 1959. 23p. tables. Project 301-664/

43006/08. CONFIDENTIAL

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Preparations by this procedure give a very pure product which has excellent thermal stability at 260°C.

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acetate

5. Methanol

acetone

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